Trends in High-Capacity Cathodes for Rechargeable Lithium Batteries

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OVERVIEW:

High capacity cathodes are key to unlocking the true potential of high capacity anode designs. This article discusses those opportunities and challenges.

Metal Oxides

Materials such as high loading NMC, excess lithium LMO, and high voltage chemistries are increasingly seen in literature but have some barriers to overcome before commercialization.

Alternative Chemistries

Chemistries such as oxygen or sulfur cathodes are being looked at for next generation research but pose some performance tradeoffs.
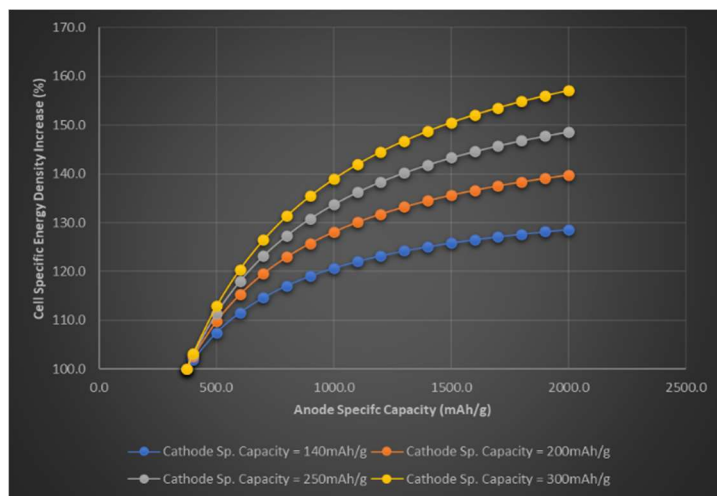
Cathodes to Unlock High Energy Density Anodes

By and large, the performance of Lithium batteries is determined by their energy storage components, the anode and the cathode materials. The physicochemical and electrochemical characteristics of these electrodes determine performance, safety, and cost characteristics of the battery. Considering the impact that Lithium-ion batteries have had on our lives, and the materials science innovations that have gone into enabling this versatile energy technology, it is no surprise that the 2019 Nobel Prize for Chemistry was awarded to three pioneers in this field. However, the quest for higher energy density batteries is far from over and is now driven largely by the imminent electrification of the global transportation fleet.

Energy storage performance of Lithium-ion electrode materials is typically gauged by (1) the specific capacity (mAh/g) of the material and (2) the voltage (V) of the electrode with respect to Lithium metal. For anodes, candidates like Silicon and Lithium are actively being investigated as high-capacity alternatives to state-of-the-art carbon (graphite) electrodes. Anode capacities potentially increase from ~370mAh/g for the benchmark graphite electrodes to 1858mAh/g (theoretical) for Silicon ($Li_{3.75}Si$) and 3800mAh/g (theoretical) for Lithium – although, practical capacities are well under 2000mAh/g. In comparison, cathode capacities have been in the 140mAh/g to 180mAh/g for the state-of-the-art Lithium Metal Oxides (LMO), thus necessitating 2X the mass of cathode material compared to anode in full cells.

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Emerging cathode materials are expected to push the specific capacity numbers to the 250-300mAh/g range, with advanced LMOs, and even higher for Sulfur and Oxygen cathodes. Assuming a nominal cell voltage of 3.7V (typical for LMO cells), Figure 1 shows how energy density improvements in Lithium-ion made due to improvements in anode capacities can be held back because of lack of improvements in cathode capacities. Using a conventional Lithium Cobalt Oxide (LiCoO2) | Graphite (C) combination as the benchmark the figure shows that a 140mAh/g cathode can cap cell energy density improvements at a ~30% ceiling regardless of anode capacity, whereas the cell energy density can improve to over 60% if the cathode specific capacity is 300mAh/g. The cell energy density improvement potential (ceiling) can be even higher for cathodes with capacities >300mAh/g.

Figure 1: Comparison of cell specific energy density as a function of anode and cathode specific capacities.

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Therefore, to truly realize the potential of emerging high-capacity anodes we need equivalent advances in high-capacity cathodes. This white paper will first review the history and state-of-the-art of high-capacity cathodes for rechargeable Lithium batteries. Following that, it will discuss emerging high-capacity cathode materials some of the challenges that researchers face in their efforts to increase cathode capacities well beyond where they are today.

General Overview of Lithium-ion Battery Cathodes

It is estimated that roughly 350 kilotons of Li-ion cathode material were produced in 2018, generating a revenue of around US$7.2B.[1] This number may have reached over 400 kilotons in 2020, and is projected to be over 1000 kilotons by 2030. One of the earliest Lithium battery cathode materials, Titanium Disulfide (TiS_2), was developed in the 1970s and stores Lithium using an *intercalation* or *insertion* mechanism.[3]

However, TiS_2 and other Metal Disulfides, were limited in performance because they had relatively low voltage (2.5V) and required pairing with Lithium metal anodes, which introduced cycle life and safety issues. Lithium Metal Oxides (LMO) cathodes were developed in the early 1980s, and to the present day continue to be the primary choice for Lithium batteries.[1] There are many different types of LMOs, each with a unique set of electrochemical characteristics, but they all store Lithium using the intercalation principle. Since LMO cathodes already contain Lithium, they can be paired with anode materials that do not contain any Lithium in the as-assembled cell. This enabled the use of Carbon (graphite) electrodes, thereby bypassing the use of Lithium metal electrodes that have safety and cycle-life issues. This was the origin of the Lithium-ion battery. Over the years, LMO cathodes have served a wide range of applications, each application having its own, unique energy density, power density, cycle life and storage life requirements. While versatile, the intercalation chemistry based LMOs are limited in their Lithium storage capabilities, and therefore their specific capacities and energy densities. Alternate materials utilizing *conversion chemistry* instead of intercalation, like Sulfur (for Lithium-Sulfur batteries) and Oxygen (for Lithium-Air batteries), have the potential to provide significantly higher energy densities. However, these materials still have significant hurdles of their own that need to be overcome before they can be used in mainstream batteries, not to mention they need to be paired with Lithium metal.[4]

Lithium Metal Oxides have been the workhorse chemistry in commercial rechargeable Lithium batteries since their introduction in the late 1980s. Four transition metals, Cobalt (Co), Nickel (Ni), Manganese (Mn) and Iron (Fe), individually or in combination, are found in a vast majority of the LMOs in either simple oxide (LiM_xO_y)or polyanionic oxide ($LiM_x(AO_z)_y$) form – where M is the metal, and A is usually a non-metallic element like Phosphorus (P) or Sulfur(S). The earliest LMOs were *layered* intercalation compounds, with the general formula $LiMO_2$, with $LiCoO_2$ (LCO) being the most popular because of its optimum performance of energy density, cycle life and structural stability. Layered LMO compounds continue to be the cathode materials of most interest today because they offer the highest capacity. Non-layered LMO structures, like *Spinel,* with general formula LiM_2O_4 were also introduced in the 1980s and have found their niche in the battery industry where high capacity is not the major requirement for the application. $LiMn_2O_4$ is a typical example. Another non-layered structure, called *Olivine*, is found primarily in the polyanionic LMOs, with $LiFePO_4$ (LFPO) being a typical example. LFPO too is used in applications that can sacrifice some energy density. However, because of their structural stability and low cost, they seen commercial success in several applications. **Table 1** lists the electrochemical characteristics of all the major Lithium cathode materials and their commercial status in the Lithium battery industry.

Table 1: *General electrochemical characteristics and status of Rechargeable Lithium Battery Cathodes*

Cathode Chemistry	Practical (Theoretical) Cathode specific capacity (mAh/g)	Voltage vs. Li (V)	Typical anode pairing	Status
Metal Sulfides	180 (240)	2.2	Lithium	No longer pursued
LMO (layered)	140 – 200 (270)	3.6 - 3.8	Carbon / Silicon	Commercial
LMO (Spinel)	120 – 130 (148)	3.8 – 4.2	Carbon / Silicon	Limited-commercial
LMO (Olivine)	160 (170)	3.2	Carbon / Silicon	Commercial
Excess-Li LMO	220 – 300	3.6	Carbon / Silicon	R&D
Sulfur	<1000 (1167)	2.2	Lithium / Silicon	R&D
Oxygen	<1000 (1790)	2.9	Lithium	R&D

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High-Capacity Lithium Metal Oxide Cathodes

Layered compounds have provided the highest energy density among LMOs, by virtue of an optimum combination of voltage and specific capacity. Early versions of layered LMOs relied primarily on Co containing materials like LiCoO2, having capacities of ~140mAh/g and charging voltages of ~4.2V (3.7V nominal). While LCO has a theoretical capacity of around 270mAh/g, only about 140mAh/g can practically be extracted from it. This is because at >140mAh/g capacities oxygen is released from the LCO structure, leading to serious safety issues. The Nickel analogue of LCO, $LiNiO_2$ (LNO), does not have this oxygen evolution issue, and can hence be charged to higher capacity values (~170mAh/g), even though its theoretical capacity is close to that of LCO. However, LNO has other issues related to capacity retention and chemical compatibility that have precluded it from being used in mainstream batteries. So, in the early days of Li-ion, LCO was preferred over LNO because the cobalt containing materials had better cycle life and were also easier to process during manufacturing. In the 1990s, practical versions of $LiNiO_2$ were developed by adding Cobalt and Aluminum (Al) as a dopant. These compounds, dubbed NCA (for Nickel Cobalt Aluminum), have the stoichiometry $LiNi_{0.80}Co_{0.15}Al_{0.05}O2$ and demonstrated specific capacities of ~180mAh/g. They were first introduced into portable electronic products and have since made their way into electric vehicles (EV). Spinel structure based LMOs like Lithium Manganese Oxides ($LiMn_2O_4$), can also be doped with Ni, to increase specific capacities in compounds such as $LiMn_{1.5}Ni_{0.5}O_4$. However, these doped compounds must be charged to higher voltages to achieve the higher specific capacities, which could introduce electrolyte degradation issues.
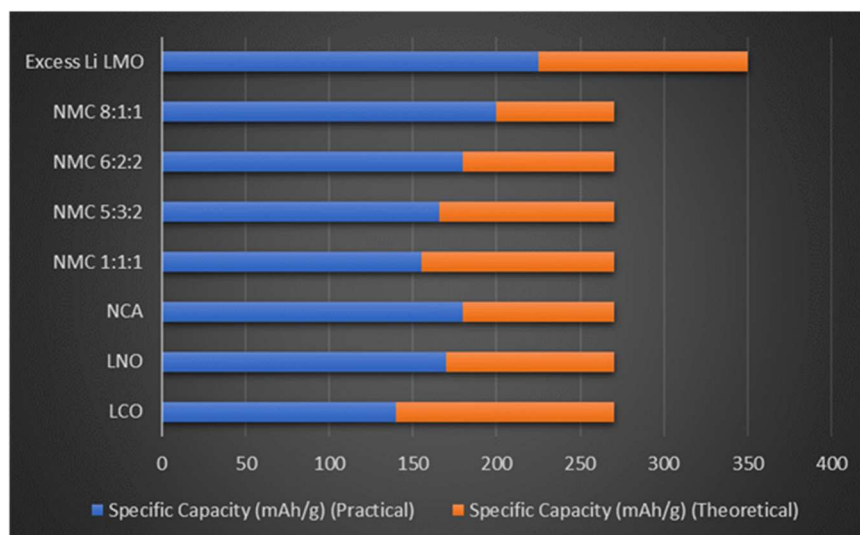
"NMC" Based Lithium Metal Oxides

Over the last 10-15 years, layered LMO compounds with the general formula $LiNi_xMn_yCo_zO_2$ (x+y+z=1) have increasingly been investigated as high-capacity cathodes.[1] This class of cathode materials, often referred to as "NMC", typically have theoretical capacities of around 270mAh/g regardless of their x, y, z values. This is because the atomic masses of Ni, Mn and Co are quite close to each other. However, just as with NCA, the structural and electrochemical stability provided by combining multiple metals in the same compound, NMCs can be charged to higher capacities without demonstrating oxygen loss (as in LCO) or cycle life issues (as in LNO). In general, higher Ni content correlates with higher Lithium extraction at a given charge voltage, thereby providing higher specific capacities. NMCs with a Ni:Mn:Co ratio of 1:1:1 (referred to as NMC 1:1:1, NMC 3:3:3 or NMC 3.33: 3.33: 3.33) were the first to be investigated in this class of compounds, and could be successfully cycled to ~155mAh/g, a significant improvement over LCO. The current state of development of NMC cathodes focuses on maximizing Ni content, while reducing Mn and Co. This trend improves energy density, while also reducing the dependance on expensive Co, which is also classified as a conflict mineral. Progressing from NMC 1:1:1, NMC 5:3:2 (~166mAh/g), NMC 6:2:2 (~180mAh/g) and NMC 8:1:1 (~200mAh/g) have all been developed and are in varying stages of commercialization in the automotive industry. Further increase in Ni content can push capacities closer to the theoretical capacity of 270mAh/g, although one would have to resolve the issues of decreased structural stability

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(due to higher Li extraction) and decreased thermal stability (due to higher Ni content.

Excess Lithium LMO Compounds

Traditional layered compounds with the general $LiMO_2$ formula have theoretical capacity of ~270mAh/g, with practical capacities typically ~200mAh/g. Another class of layered compounds with so-called "excess Lithium" compositions have delivered initial capacities in the 220-300mAh/g. The higher capacity is believed to arise from phases with higher Lithium content, like Li_2MO_3, that can contribute more than 1 Lithium to the energy storge process.[5] While promising, to date, these materials still suffer from issues related to voltage fade and cycle-life. Most of the development efforts in excess-Lithium layered cathodes now focus on mitigating these issues. One approach is to use new metal substituents in the layered structure that can stabilize the material over long-term cycling. Another approach is to develop spherical cathode particles with core-shell morphologies, or even gradient structures, where shell structures are of proven stable NMC type compositions and the core is composed of high-capacity excess Lithium compositions.[5] If the voltage-fade and cycle-life issues of this class of cathodes are resolved, they may well follow NMC 8:1:1 on the Lithium battery cathode roadmap. As with NMC cathodes, higher charge voltages in the excess Lithium compounds can lead to higher capacities. However, invoking higher charge voltages is non-trivial, since it can lead to poor cycle life and storage life performance of the cell.[6] **Error! Reference source not found.** 2 charts the practical and theoretical capacities for the commercial and emerging Lithium Metal Oxide cathode materials and compares them to the conventional LCO and LNO materials.

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Figure 2: *Practical and theoretical specific capacities for layered Lithium Metal Oxide cathodes[1]*

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High Voltage Cathodes and Role of electrolyte

The lowest unoccupied molecular orbital (LUMO) of the common non-aqueous Lithium battery electrolytes lies below the Li+/Li electrochemical potential. This leads to a reduction of the electrolyte when the electrolyte and lithiated anode or lithium metal come in contact with each other. However, this issue is mitigated once some of the byproducts from the early stages of the electrolyte degradation process form a passivation layer called the *solid electrolyte interphase* (SEI) layer on the anode, thereby preventing further electrolyte reduction. Similarly, on the cathode side, if the highest occupied molecular orbital (HOMO) of the electrolyte is higher than the electrochemical potential of the cathode, it can undergo oxidative decomposition.[1] This is not an issue if charge voltages are held below 4.3V. But if charge voltages of >4.3V are required, as they would be for high-voltage cathodes like the NMCs and the excess-Lithium materials, electrolyte decomposition becomes a serious limitation. One approach to prevent electrolyte decomposition at higher voltages is to create an SEI layer on the cathode, much like the one created on the anode for lower voltage stabilization. Researchers are improving current electrolyte formulations using additives (e.g., 1,3-Propane sulfone) that promote cathode SEI formation.[1] In the longer term, organic solvents and Lithium salts that are stable over wider voltage windows are desired. For example, eliminating ethylene carbonate (EC), a key component of conventional Lithium battery electrolytes, was found to improve the performance of Lithium batteries at voltages greater than 4.3V.[6] Some solid-state electrolytes being developed by solid-state lithium battery developers may also have wider voltage stability windows. Although, to be viable, these solid-state electrolytes will need to have high enough ionic conductivities to be practical for mainstream Lithium battery applications.[1]

Electrode fabrication trends

While the chemical composition of the cathode material will primarily determine the potential limits of cell performance, efficient conversion of these cathode materials (powders) into sheet electrodes will determine how well we can harness the performance potential. Electrode parameters like length, thickness, active material loading and density/porosity etc. need to be tailored to optimize the energy density and power density of the battery to suit the application. Shorter, thicker electrodes provide the highest packing density of the electrode material in the cell, thereby optimizing energy density. However, this may come at the cost of power density (rate capability) and cycle life. Thicker electrodes are also difficult to hold together, as they may crack and delaminate from the current collector during cycling.

Electrodes are typically fabricated using a slurry casting process. Several advances continue to be explored in slurry formulations and the casting process. Dry electrode processing, without any solvents, have been proposed but have not yet been implemented in Lithium battery manufacturing.[1] New binders that improve cohesive strength and better accommodate volume changes in the electrodes during cycling can help extend cycle life.[8] Adhesion promotion layers between the electrode and current collector can also prevent delamination,

reduce interfacial impedance and improve cycle life and rate-capability.[8]   Recently, electrode sheets are also being coated with thin layers of metal oxides (e.g. Al_2O_3, CeO_2 etc.) to stabilize the surface of the electrode particles and provide extended cycling.[11]

Alternate Cathode Chemistries

Two cathode chemistries, Sulfur (S) and Oxygen (O2) are often cited on most Lithium battery roadmaps, as possible candidates for high-capacity cathodes to follow LMOs. These candidates have been known to battery researchers since the early days of rechargeable Lithium batteries. Several issues associated with each of these materials have yet to be resolved. Both materials are best suited for use with Lithium metal anodes, rather than with other Li-ion cathodes. So, in addition to any cathode related issues, one must also resolve the issues associated with Lithium anodes. The central issue related to Lithium anode is that it forms dendrites during charging, which leads to poor cycle life and safety issues. Several approaches are being explored to resolve this issue.[7]

Sulfur

Sulfur cathodes in Lithium-Sulfur batteries operate according to the electrochemical reaction: $2\ Li + S \rightarrow Li2S$. The theoretical specific capacity of Sulfur per this 2-electron transfer reaction is around 1167mAh/g 1675mAh/g, using Li_2S and S basis respectively. When coupled with Lithium metal, which has the specific capacity of 3860mAh/g, a 2.2V battery is formed with a theoretical energy density of 2570Wh/kg. It is therefore not surprising that there is so much interest in Lithium-Sulfur batteries. However, before we get anywhere close to realizing this energy density, several issues related to cycle life need to be resolved.[4] Also, since sulfur-based batteries have lower voltages, they will require significantly different configurations compared to conventional Lithium-ion, to meet the voltage and capacity requirements of the application. Last but not least, Lithium sulfur batteries need to address the system-level issues related to safety that is introduced by using Lithium metal as the anode. There is a significant amount of development work that is taking place in Lithium-Sulfur batteries, and compared to Lithium-air, the sulfur-based systems have a much higher likelihood of commercialization in the next 3-5 years in niche applications. Mainstream applications will take longer to happen.

Oxygen

Oxygen cathodes in Lithium-Oxygen or Lithium-air batteries function according to the electrochemical equation: $2\ Li + \frac{1}{2}\ O2 \rightarrow Li2O$. The theoretical capacity for the oxygen cathode is around 1790mAh/g and 3350mAh/g, using Li_2O and O ($\frac{1}{2}O_2$) basis respectively. With the Lithium metal anode demonstrating a specific capacity of 3860mAh/g, a 2.9V battery is formed, with the theoretical energy density estimated to be 5200Wh/kg.[1] The most studied version of the Lithium-Oxygen battery is the Lithium-air battery, wherein the oxygen is provided by ambient air. The operation of the Lithium-air battery is similar to the operation of other metal-air batteries such as Zinc-air and Aluminum-air batteries. So, the air-cathode related challenges in developing Lithium-air are like those that are encountered in Metal-air and fuel cell systems. For example, the cost and power density issues, related to the support materials and catalysts required for the air-cathode need to be addressed. As with the Li-S systems, the cycle life and safety issues related to recharging the Lithium anode also need to be resolved. At the present time, there are few development efforts focusing on Li-air batteries for mainstream applications.

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Concluding Remarks

Lithium metal oxides, specifically the layered versions, have been commercial in Lithium batteries since the early 1990s and will continue to be so for at least the next 5-10 years. The transition from $LiMO_2$ compositions primarily based on Cobalt to ones that are richer in Ni is well underway. This transition is driven by industry requirements for higher capacity (energy density) and lower cost, not to mention the desire to move away from using conflict-minerals in the battery supply chain. NMC compositions continue to move from the balanced NMC 1:1:1 to the higher nickel NMC 8:1:1 version, as they approach the theoretical capacity thresholds of around 270mAh/g. Further increases in capacities with LMO materials will require a transition to excess Lithium compositions that contribute more than one Lithium per molecule for Lithium-ion storage. If the voltage-fade and cycle-life issues can be resolved, these materials will enable capacities of up to 300mAh/g. Viable versions of excess Lithium compounds could emerge in the next 3-5 years, although at a cost premium associated with the exotic structures they may require, to resolve voltage fade and cycle-life issues. Further increase in cathode capacities will require a move to conversion electrodes like Sulfur and Oxygen. Sulfur electrodes are a lot further along in the development cycle. Even so, it may be 5-10 years before they go mainstream. Concurrent with the advances in the compositions of the cathodes, advances in high-voltage electrolytes, anode compositions and electrode fabrication methods will play an important role in next generation Lithium batteries.

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